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METHOD FOR REFORMING CARBON BLACK

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Abstract

PURPOSE: To reform carbon black to have excellent properties as an electrically conductive material, by heat-treating carbon black in the presence of a specified compd. in an inert atmosphere.

CONSTITUTION: Carbon black (pref. one having a large surface area, pref. $800\text{m}^2/\text{g}$ or above, DBP absorption of $250\text{ml}/100\text{g}$ or above and high electrical conductivity) is heat-treated at $250\text{--}800^\circ\text{C}$ in the presence of a higher fatty acid (e.g. palmitic or oleic acid), a base (e.g. lutidine), an arom. compd. (e.g. t-stilbene), an ester (e.g. tristearin), a sulfur compd. (e.g. diphenyl disulfide) or a polyol (e.g. polyglycerol) and air-cooled, thus obtaining reformed carbon black having excellent properties as an electrically conductive material. It is desirable that when raw carbon black contains a large quantity of metal, it is treated with a mineral acid to remove the metal.

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METHOD FOR THE MODIFICATION OF CARBON BLACK

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Claims

1. A method for the modification of carbon black, characterized by the fact that carbon black is subjected to a heat treatment at a temperature of 250-800°C under an inert gas

atmosphere in the presence of a higher fatty acid, a base, an aromatic compound, an ester, a sulfur-containing compound or a polyol.

2. The method described in Claim 1, in which carbon black is treated with a mineral acid prior to said treatment.

3. The method described in Claim 1, in which carbon black is treated with a mineral acid after said treatment.

Detailed explanation of the invention

The present invention relates to a quality-improving method for carbon black (also called CB hereafter).

Recently, applications of CB have been developed for high-voltage cables, surface heaters, communication cables, magnetic tapes, video disks, electromagnetic-wave-shielding materials, electrostatic inhibiting materials, electrically conductive coating materials, xerographic toners, and other organic electrically conductive materials.

During the development of these new materials, it is an important task to render characteristics by the optimal control and design of physical and chemical mechanisms of polymers, monomers, or other compounds to be blended with CB, not to mention CB itself.

It is preferable that CB for use in the applications mentioned previously be CB with a high electrical conductivity. For example, acetylene black, conductive furnace black, channel black, partial oxidation method gas process by-product carbon black and so on can be exemplified.

Acetylene black is obtained from high-purity acetylene gas by the thermal process or the furnace process. Conductive furnace black is black with a high specific surface area and a high oil absorption amount (DBP) obtained by the furnace process. In particular, primary particle diameters are relatively small and porous- or eggshell-type particles are contained to a large extent. In the case of the development of a structure with the fusion of tens to hundreds of these particles, a high electrical conductivity is discovered even in a resin. Channel black is CB obtained by the channel process. The by-product CB is CB obtained from an oily raw material during the generation of water vapor or the like by partial combustion.

These CBs contain small amounts of hydrogen and oxygen. They are present as functional groups on the surface of the CB or near the surface. For example, phenol ($>\text{OH}$, weakly acidic), quinone ($>=\text{O}$), carboxylic acid ($>\text{COOH}$, strongly acidic), lactone ($>\text{COO}-$), active hydrogen ($>\text{-H}$) and so on are available. These generally trap electrons and function in a direction to decrease the electrical conductivity. They are considered to render an effect on the affinity during mixing with a resin or molding.

During kneading of a resin, especially PVC, with a CB of a high structure, self-heat generation occurs and the pyrolysis of the PVC is promoted, leading to the deterioration in the quality of molded products.

In order to adjust the quality, depending on the type of CB, a trace amount of metal salt and so on is added, or these enter during the manufacturing process. They often render an undesirable effect on the materials. The removal of this metal can be achieved by an acid treatment. However, this causes a reduction in the pH of the CB. For example, in the case of kneading with PVC, the stability of the PVC is decreased.

As a result of investigations on the method for the manufacture of the CB having excellent properties as an electrically conductive material, it has been discovered that CB that is excellent as an electrically conductive material can be obtained if the CB is subjected to a heat treatment at a temperature of 250-800°C, preferably 300-400°C, for 1-10 h under an inert gas atmosphere in the presence of a higher fatty acid, a base, an aromatic compound, an ester, a sulfur-containing compound or a polyol.

As the CB for use as a raw material, any CB used as a raw material can be used. For example, the CBs described previously can be used. Preferably, a CB with a high electrical conductivity having a large surface area, preferably at least 800 m²/g, and a DBP oil absorption amount of at least 250 mL/100 g, can be used.

In the case in which the CB contains a large amount of a metal, prior to the heat treatment, the CB is treated with a mineral acid, such as hydrochloric acid, sulfuric acid or the like, to carry out the metal removal. Alternatively, the heat treatment is first conducted and then the metal removal is carried out. This treatment is generally conducted at a concentration of 1-10% for 1-10 h and, if necessary, at a temperature of 200°C or lower. After the treatment, water washing is conducted. If necessary, it may be neutralized with an aqueous ammonia solution or the like, and then washed with water.

As the higher fatty acids, fatty acids with 7-23 carbon atoms, such as palmitic acid, lauric acid, isostearic acid, 1,2-hydroxystearic acid, behenic acid, caprylic acid and other saturated fatty acids, oleic acid and other unsaturated fatty acids can be used.

As the bases, 2,3-benzopyridine, lutidine, stearyl amine, indole, hexamethylenediamine, triethanolamine, 1,3-diphenylguanidine, ammonia, ammonia and stearic acid, ϵ -caprolactam, melamine, diphenylthiourea, glutamic acid and so on can be mentioned.

As the aromatic compounds, t-stilbene, α -phenylcinnamic acid, methyl cinnamate, styrene, biphenyl, anthracene, bisphenol A and so on can be mentioned. As the esters, triallyl trimellitate, glycerol monostearate, tristearin, PEG monostearate, stearyl ricinolate, monomethyl maleate and so on can be mentioned. As the sulfur-containing compounds, octadecyl thiodiglycolate, diphenyl disulfide, benzothiophene, 2-naphthalenethiol,

2-mercaptobenzothiazole, 4,4'-dithiomorpholine, tetramethylthiuram disulfide and so on can be mentioned. As the polyols, polyglycerol, 1,6-hexanediol and so on can be mentioned.

These are used at 1-10% of the CB.

Prior to the heat treatment, the CB and the previously mentioned additive compounds are generally mixed well and then subjected to the heat treatment. If necessary, they can be used during mixing with a solvent. As a treating apparatus, for example, a rotary kiln can be used.

After the heat treatment, the desired material can be obtained by natural cooling.

By the method of the present invention, the modified CB having excellent properties can be obtained. Its mechanism of action is unclear. However, it is presumed that functional groups as described previously are present on the CB surface. By the treatment of the present invention, they are partially decarboxylated and decomposed, and partially esterified to improve the pH. The active sites on the surface of the CB are decreased and affinity with respect to the resin is increased. In particular, it is presumed that, by mixing with the resin and molding, a good effect is rendered to the surface activity of the electrically conductive material obtained.

The embodiments of the present invention will be explained with application examples.

Application Example 1

In a 100-L glass flask, 60 kg of 5% hydrochloric acid were introduced and 3 kg of the carbon black (Black Pearl [transliteration] 2000, manufactured by Cabot Co.) shown in Table 1 were also introduced and gently stirred at 95°C for 6 h. After cooling, it was filtered. Water washing was repeated until the chloride ion concentration in the filtrate was 10 ppm or less. The pH was brought to 10 by the addition of a 5% aqueous ammonia solution. The filtration and the water wash were repeated until the chloride ion concentration was 1 ppm or less. The filtration sludge was dried under vacuum to obtain demetallized carbon black. The physical properties of the carbon black obtained are shown in Table 1.

Table 1

	①	②
	原料CB	处理CB
③ DBP吸油量 (ml/100g)	315	300
④ 水分 (%)	0.95	0.05
⑤ pH	9.6	5.8
⑥ 体积电阻率 (Ω·cm) ***	7.5	1.8
⑦ 热稳定性 (分/℃) ***	8.0/192°	7.0/185°

Key: 1 Raw material CB
2 Treated CB

- 3 DBP oil absorption amount (mL/100 g)
- 4 Ash content (%)
- 5 Volume resistivity (Ω cm)⁽¹⁾
- 6 Dynamic thermal stability (min/°C)⁽²⁾

⁽¹⁾ The volume resistivity value for a sheet obtained by

thoroughly mixing PVC Zeon 400 x 150 p 100 parts

Dibutyltin dilaurate 1.0

Dibutyltin maleate 4.0

Epoxidized soybean oil 1.0

Barium stearate 1.0

Stearic acid 1.0

CB (Black Pearl 2000, manufactured by Cabot Co.) 20

kneading it at 150°C for 7 min, and pressing it at 180°C and 110 kg/cm².

⁽²⁾ The value measured with a Brabender Co. plastograph after the micropulverization of the sheet described in ⁽¹⁾.

Application Example 2

The treated CB obtained in Application Example 1 was introduced into an electric heating type rotary kiln. Under a nitrogen gas stream, the heat treatment was conducted in the presence of the additive shown in Table 2. The CB obtained was analyzed and the results are shown in Table 2.

Table 2

①	②	③	④	⑤	
添 加 剤 (各 5%)	処理温度 (°C)	pH	全酸量 * (mg/g)	体積固有抵抗 (Ω cm)	熱安定性 (分/100°C)
イソステアリン酸	350	9.3	40	11.0	8.0/192
パルミチン酸	330	7.9	64	9.6	9.5/189
ラウリン酸	350	9.3	53	9.4	10.0/191
カプリル酸	330		68	10.5	9.0/190
ベヘン酸	330	7.7	68	11.5	10.0/192
オレイン酸	330	8.5	71	10.8	9.0/192
1,2-ビス(4-tert-ブチル ステアリン酸	350	9.3	51	11.5	12.0/192.5

*Total acid amount measuring method

Key: 1 Additive (5% each)
2 Treating temperature (°C)

- 3 Total acid amount* ($\mu\text{eq/g}$)
- 4 Volume resistivity ($\Omega \text{ cm}$)
- 5 Thermal stability (min/degree)
- 6 Isostearic acid
- Palmitic acid
- Lauric acid
- Caprylic acid
- Behenic acid
- Oleic acid
- 1,2-Hydroxystearic acid

2 g of a sample were accurately weighed, placed in a 200-mL vessel, 50 mL of a 0.01N NaOH solution were added, and the vessel was tightly plugged and shaken with a shaking machine for 4 h. Afterwards, solids were filtered off. The filtrate was titrated by neutralization with hydrochloric acid.

Application Example 3

The heat treatment of the mineral-acid-treated CB obtained in Application Example 1 was conducted by the same method as in Application Example 2 in the presence of 2,3-benzopyridine. The physical properties of the CB obtained are shown in Table 3.

Table 3

①	②	③	④	⑤	
添加量 (%)	処理温度 (℃)	pH	全酸量	降電阻有法 ($\Omega \text{ cm}$)	熱安定性
1.0	330	7.7	94	8.0	12.0/187
3.3*	330	6.7	74	9.6	20.5/191
5.0	250	7.3	200	8.9	16.5/190
"	330	9.4	40	9.3	19.0/207.5
"	400	9.0	50	8.4	16.5/195
10.0	330	6.2	50	9.4	20.5/210

* In this example, 2,3-benzopyridine was dissolved in the CB slurry after mineral acid treatment, water washing, neutralization and water washing. The CB after mixing, filtration and vacuum drying was subjected to the heat treatment without the addition of the new additive.

- Key:
- 1 Amount added (%)
 - 2 Treating temperature ($^{\circ}\text{C}$)
 - 3 Total acid amount
 - 4 Volume resistivity ($\Omega \text{ cm}$)
 - 5 Thermal stability

Application Example 4

The same implementation was conducted as in Application Example 3 except that the additive shown in Table 4 was used instead of the 2,3-benzopyridine of Application Example 3. The results are shown in Table 4.

Table 4

①	②	③	④	⑤	
添加剤 (%)	処理温度 (℃)	pH	全残量	体積百分率 (%)	安定性
ルチン	330	8.7	69	10.6	12.0/194
ステアリン酸 アミン	330	9.4	41	11.1	9.0/194
インドール	330	8.7	71	10.4	10.5/191
ヘキサメチレン ジアミン	330	8.7	59	11.0	9.5/190
トリエタノール アミン	330	8.1	60	10.0	14.0/193
1,3-ジフェニル プロパン	350	8.9	53	12.6	10.0/191
アノニウム	330	9.3	39	8.5	11.0/194
アノニウム 塩	350	9.7	40	8.5	15.0/192
⑥ ⑧ ⑨ ⑩ ⑪ ⑫ ⑬ ⑭ ⑮ ⑯ ⑰ ⑱ ⑲ ⑳ ㉑ ㉒ ㉓ ㉔ ㉕ ㉖ ㉗ ㉘ ㉙ ㉚ ㉛ ㉜ ㉝ ㉞ ㉟ ㊱ ㊲ ㊳ ㊴ ㊵ ㊶ ㊷ ㊸ ㊹ ㊺ ㊻ ㊼ ㊽ ㊾ ㊿ ㋀ ㋁ ㋂ ㋃ ㋄ ㋅ ㋆ ㋇ ㋈ ㋉ ㋊ ㋋ ㋌ ㋍ ㋎ ㋏ ㋐ ㋑ ㋒ ㋓ ㋔ ㋕ ㋖ ㋗ ㋘ ㋙ ㋚ ㋛ ㋜ ㋝ ㋞ ㋟ ㋠ ㋡ ㋢ ㋣ ㋤ ㋥ ㋦ ㋧ ㋨ ㋩ ㋪ ㋫ ㋬ ㋭ ㋮ ㋯ ㋰ ㋱ ㋲ ㋳ ㋴ ㋵ ㋶ ㋷ ㋸ ㋹ ㋺ ㋻ ㋼ ㋽ ㋾ ㋿ ㌀ ㌁ ㌂ ㌃ ㌄ ㌅ ㌆ ㌇ ㌈ ㌉ ㌊ ㌋ ㌌ ㌍ ㌎ ㌏ ㌐ ㌑ ㌒ ㌓ ㌔ ㌕ ㌖ ㌗ ㌘ ㌙ ㌚ ㌛ ㌜ ㌝ ㌞ ㌟ ㌠ ㌡ ㌢ ㌣ ㌤ ㌥ ㌦ ㌧ ㌨ ㌩ ㌪ ㌫ ㌬ ㌭ ㌮ ㌯ ㌰ ㌱ ㌲ ㌳ ㌴ ㌵ ㌶ ㌷ ㌸ ㌹ ㌺ ㌻ ㌼ ㌽ ㌾ ㌿ ㍀ ㍁ ㍂ ㍃ ㍄ ㍅ ㍆ ㍇ ㍈ ㍉ ㍊ ㍋ ㍌ ㍍ ㍎ ㍏ ㍐ ㍑ ㍒ ㍓ ㍔ ㍕ ㍖ ㍗ ㍘ ㍙ ㍚ ㍛ ㍜ ㍝ ㍞ ㍟ ㍠ ㍡ ㍢ ㍣ ㍤ ㍥ ㍦ ㍧ ㍨ ㍩ ㍪ ㍫ ㍬ ㍭ ㍮ ㍯ ㍰ ㍱ ㍲ ㍳ ㍴ ㍵ ㍶ ㍷ ㍸ ㍹ ㍺ ㍻ ㍼ ㍽ ㍾ ㍿ ㏀ ㏁ ㏂ ㏃ ㏄ ㏅ ㏆ ㏇ ㏈ ㏉ ㏊ ㏋ ㏌ ㏍ ㏎ ㏏ ㏐ ㏑ ㏒ ㏓ ㏔ ㏕ ㏖ ㏗ ㏘ ㏙ ㏚ ㏛ ㏜ ㏝ ㏞ ㏟ ㏠ ㏡ ㏢ ㏣ ㏤ ㏥ ㏦ ㏧ ㏨ ㏩ ㏪ ㏫ ㏬ ㏭ ㏮ ㏯ ㏰ ㏱ ㏲ ㏳ ㏴ ㏵ ㏶ ㏷ ㏸ ㏹ ㏺ ㏻ ㏼ ㏽ ㏾ ㏿ 㐀 㐁 㐂 㐃 㐄 㐅 㐆 㐇 㐈 㐉 㐊 㐋 㐌 㐍 㐎 㐏 㐐 㐑 㐒 㐓 㐔 㐕 㐖 㐗 㐘 㐙 㐚 㐛 㐜 㐝 㐞 㐟 㐠 㐡 㐢 㐣 㐤 㐥 㐦 㐧 㐨 㐩 㐪 㐫 㐬 㐭 㐮 㐯 㐰 㐱 㐲 㐳 㐴 㐵 㐶 㐷 㐸 㐹 㐺 㐻 㐼 㐽 㐾 㐿 㑀 㑁 㑂 㑃 㑄 㑅 㑆 㑇 㑈 㑉 㑊 㑋 㑌 㑍 㑎 㑏 㑐 㑑 㑒 㑓 㑔 㑕 㑖 㑗 㑘 㑙 㑚 㑛 㑜 㑝 㑞 㑟 㑠 㑡 㑢 㑣 㑤 㑥 㑦 㑧 㑨 㑩 㑪 㑫 㑬 㑭 㑮 㑯 㑰 㑱 㑲 㑳 㑴 㑵 㑶 㑷 㑸 㑹 㑺 㑻 㑼 㑽 㑾 㑿 㒀 㒁 㒂 㒃 㒄 㒅 㒆 㒇 㒈 㒉 㒊 㒋 㒌 㒍 㒎 㒏 㒐 㒑 㒒 㒓 㒔 㒕 㒖 㒗 㒘 㒙 㒚 㒛 㒜 㒝 㒞 㒟 㒠 㒡 㒢 㒣 㒤 㒥 㒦 㒧 㒨 㒩 㒪 㒫 㒬 㒭 㒮 㒯 㒰 㒱 㒲 㒳 㒴 㒵 㒶 㒷 㒸 㒹 㒺 㒻 㒼 㒽 㒾 㒿 㓀 㓁 㓂 㓃 㓄 㓅 㓆 㓇 㓈 㓉 㓊 㓋 㓌 㓍 㓎 㓏 㓐 㓑 㓒 㓓 㓔 㓕 㓖 㓗 㓘 㓙 㓚 㓛 㓜 㓝 㓞 㓟 㓠 㓡 㓢 㓣 㓤 㓥 㓦 㓧 㓨 㓩 㓪 㓫 㓬 㓭 㓮 㓯 㓰 㓱 㓲 㓳 㓴 㓵 㓶 㓷 㓸 㓹 㓺 㓻 㓼 㓽 㓾 㓿 㔀 㔁 㔂 㔃 㔄 㔅 㔆 㔇 㔈 㔉 㔊 㔋 㔌 㔍 㔎 㔏 㔐 㔑 㔒 㔓 㔔 㔕 㔖 㔗 㔘 㔙 㔚 㔛 㔜 㔝 㔞 㔟 㔠 㔡 㔢 㔣 㔤 㔥 㔦 㔧 㔨 㔩 㔪 㔫 㔬 㔭 㔮 㔯 㔰 㔱 㔲 㔳 㔴 㔵 㔶 㔷 㔸 㔹 㔺 㔻 㔼 㔽 㔾 㔿 㕀 㕁 㕂 㕃 㕄 㕅 㕆 㕇 㕈 㕉 㕊 㕋 㕌 㕍 㕎 㕏 㕐 㕑 㕒 㕓 㕔 㕕 㕖 㕗 㕘 㕙 㕚 㕛 㕜 㕝 㕞 㕟 㕠 㕡 㕢 㕣 㕤 㕥 㕦 㕧 㕨 㕩 㕪 㕫 㕬 㕭 㕮 㕯 㕰 㕱 㕲 㕳 㕴 㕵 㕶 㕷 㕸 㕹 㕺 㕻 㕼 㕽 㕾 㕿 㖀 㖁 㖂 㖃 㖄 㖅 㖆 㖇 㖈 㖉 㖊 㖋 㖌 㖍 㖎 㖏 㖐 㖑 㖒 㖓 㖔 㖕 㖖 㖗 㖘 㖙 㖚 㖛 㖜 㖝 㖞 㖟 㖠 㖡 㖢 㖣 㖤 㖥 㖦 㖧 㖨 㖩 㖪 㖫 㖬 㖭 㖮 㖯 㖰 㖱 㖲 㖳 㖴 㖵 㖶 㖷 㖸 㖹 㖺 㖻 㖼 㖽 㖾 㖿 㗀 㗁 㗂 㗃 㗄 㗅 㗆 㗇 㗈 㗉 㗊 㗋 㗌 㗍 㗎 㗏 㗐 㗑 㗒 㗓 㗔 㗕 㗖 㗗 㗘 㗙 㗚 㗛 㗜 㗝 㗞 㗟 㗠 㗡 㗢 㗣 㗤 㗥 㗦 㗧 㗨 㗩 㗪 㗫 㗬 㗭 㗮 㗯 㗰 㗱 㗲 㗳 㗴 㗵 㗶 㗷 㗸 㗹 㗺 㗻 㗼 㗽 㗾 㗿 㘀 㘁 㘂 㘃 㘄 㘅 㘆 㘇 㘈 㘉 㘊 㘋 㘌 㘍 㘎 㘏 㘐 㘑 㘒 㘓 㘔 㘕 㘖 㘗 㘘 㘙 㘚 㘛 㘜 㘝 㘞 㘟 㘠 㘡 㘢 㘣 㘤 㘥 㘦 㘧 㘨 㘩 㘪 㘫 㘬 㘭 㘮 㘯 㘰 㘱 㘲 㘳 㘴 㘵 㘶 㘷 㘸 㘹 㘺 㘻 㘼 㘽 㘾 㘿 㙀 㙁 㙂 㙃 㙄 㙅 㙆 㙇 㙈 㙉 㙊 㙋 㙌 㙍 㙎 㙏 㙐 㙑 㙒 㙓 㙔 㙕 㙖 㙗 㙘 㙙 㙚 㙛 㙜 㙝 㙞 㙟 㙠 㙡 㙢 㙣 㙤 㙥 㙦 㙧 㙨 㙩 㙪 㙫 㙬 㙭 㙮 㙯 㙰 㙱 㙲 㙳 㙴 㙵 㙶 㙷 㙸 㙹 㙺 㙻 㙼 㙽 㙾 㙿 㚀 㚁 㚂 㚃 㚄 㚅 㚆 㚇 㚈 㚉 㚊 㚋 㚌 㚍 㚎 㚏 㚐 㚑 㚒 㚓 㚔 㚕 㚖 㚗 㚘 㚙 㚚 㚛 㚜 㚝 㚞 㚟 㚠 㚡 㚢 㚣 㚤 㚥 㚦 㚧 㚨 㚩 㚪 㚫 㚬 㚭 㚮 㚯 㚰 㚱 㚲 㚳 㚴 㚵 㚶 㚷 㚸 㚹 㚺 㚻 㚼 㚽 㚾 㚿 㜀 㜁 㜂 㜃 㜄 㜅 㜆 㜇 㜈 㜉 㜊 㜋 㜌 㜍 㜎 㜏 㜐 㜑 㜒 㜓 㜔 㜕 㜖 㜗 㜘 㜙 㜚 㜛 㜜 㜝 㜞 㜟 㜠 㜡 㜢 㜣 㜤 㜥 㜦 㜧 㜨 㜩 㜪 㜫 㜬 㜭 㜮 㜯 㜰 㜱 㜲 㜳 㜴 㜵 㜶 㜷 㜸 㜹 㜺 㜻 㜼 㜽 㜾 㜿 㝀 㝁 㝂 㝃 㝄 㝅 㝆 㝇 㝈 㝉 㝊 㝋 㝌 㝍 㝎 㝏 㝐 㝑 㝒 㝓 㝔 㝕 㝖 㝗 㝘 㝙 㝚 㝛 㝜 㝝 㝞 㝟 㝠 㝡 㝢 㝣 㝤 㝥 㝦 㝧 㝨 㝩 㝪 㝫 㝬 㝭 㝮 㝯 㝰 㝱 㝲 㝳 㝴 㝵 㝶 㝷 㝸 㝹 㝺 㝻 㝼 㝽 㝾 㝿 㞀 㞁 㞂 㞃 㞄 㞅 㞆 㞇 㞈 㞉 㞊 㞋 㞌 㞍 㞎 㞏 㞐 㞑 㞒 㞓 㞔 㞕 㞖 㞗 㞘 㞙 㞚 㞛 㞜 㞝 㞞 㞟 㞠 㞡 㞢 㞣 㞤 㞥 㞦 㞧 㞨 㞩 㞪 㞫 㞬 㞭 㞮 㞯 㞰 㞱 㞲 㞳 㞴 㞵 㞶 㞷 㞸 㞹 㞺 㞻 㞼 㞽 㞾 㞿 ㏟ 㞰 㞱 㞲 㞳 㞴 㞵 㞶 㞷 㞸 㞹 㞺 㞻 㞼 㞽 㞾 㞿 㠀 㠁 㠂 㠃 㠄 㠅 㠆 㠇 㠈 㠉 㠊 㠋 㠌 㠍 㠎 㠏 㠐 㠑 㠒 㠓 㠔 㠕 㠖 㠗 㠘 㠙 㠚 㠛 㠜 㠝 㠞 㠟 㠠 㠡 㠢 㠣 㠤 㠥 㠦 㠧 㠨 㠩 㠪 㠫 㠬 㠭 㠮 㠯 㠰 㠱 㠲 㠳 㠴 㠵 㠶 㠷 㠸 㠹 㠺 㠻 㠼 㠽 㠾 㠿 㡀 㡁 㡂 㡃 㡄 㡅 㡆 㡇 㡈 㡉 㡊 㡋 㡌 㡍 㡎 㡏 㡐 㡑 㡒 㡓 㡔 㡕 㡖 㡗 㡘 㡙 㡚 㡛 㡜 㡝 㡞 㡟 㡠 㡡 㡢 㡣 㡤 㡥 㡦 㡧 㡨 㡩 㡪 㡫 㡬 㡭 㡮 㡯 㡰 㡱 㡲 㡳 㡴 㡵 㡶 㡷 㡸 㡹 㡺 㡻 㡼 㡽 㡾 㡿 㢀 㢁 㢂 㢃 㢄 㢅 㢆 㢇 㢈 㢉 㢊 㢋 㢌 㢍 㢎 㢏 㢐 㢑 㢒 㢓 㢔 㢕 㢖 㢗 㢘 㢙 㢚 㢛 㢜 㢝 㢞 㢟 㢠 㢡 㢢 㢣 㢤 㢥 㢦 㢧 㢨 㢩 㢪 㢫 㢬 㢭 㢮 㢯 㢰 㢱 㢲 㢳 㢴 㢵 㢶 㢷 㢸 㢹 㢺 㢻 㢼 㢽 㢾 㢿 㣀 㣁 㣂 㣃 㣄 㣅 㣆 㣇 㣈 㣉 㣊 㣋 㣌 㣍 㣎 㣏 㣐 㣑 㣒 㣓 㣔 㣕 㣖 㣗 㣘 㣙 㣚 㣛 㣜 㣝 㣞 㣟 㣠 㣡 㣢 㣣 㣤 㣥 㣦 㣧 㣨 㣩 㣪 㣫 㣬 㣭 㣮 㣯 㣰 㣱 㣲 㣳 㣴 㣵 㣶 㣷 㣸 㣹 㣺 㣻 㣼 㣽 㣾 㣿 㤀 㤁 㤂 㤃 㤄 㤅 㤆 㤇 㤈 㤉 㤊 㤋 㤌 㤍 㤎 㤏 㤐 㤑 㤒 㤓 㤔 㤕 㤖 㤗 㤘 㤙 㤚 㤛 㤜 㤝 㤞 㤟 㤠 㤡 㤢 㤣 㤤 㤥 㤦 㤧 㤨 㤩 㤪 㤫 㤬 㤭 㤮 㤯 㤰 㤱 㤲 㤳 㤴 㤵 㤶 㤷 㤸 㤹 㤺 㤻 㤼 㤽 㤾 㤿 㥀 㥁 㥂 㥃 㥄 㥅 㥆 㥇 㥈 㥉 㥊 㥋 㥌 㥍 㥎 㥏 㥐 㥑 㥒 㥓 㥔 㥕 㥖 㥗 㥘 㥙 㥚 㥛 㥜 㥝 㥞 㥟 㥠 㥡 㥢 㥣 㥤 㥥 㥦 㥧 㥨 㥩 㥪 㥫 㥬 㥭 㥮 㥯 㥰 㥱 㥲 㥳 㥴 㥵 㥶 㥷 㥸 㥹 㥺 㥻 㥼 㥽 㥾 㥿 㦀 㦁 㦂 㦃 㦄 㦅 㦆 㦇 㦈 㦉 㦊 㦋 㦌 㦍 㦎 㦏 㦐 㦑 㦒 㦓 㦔 㦕 㦖 㦗 㦘 㦙 㦚 㦛 㦜 㦝 㦞 㦟 㦠 㦡 㦢 㦣 㦤 㦥 㦦 㦧 㦨 㦩 㦪 㦫 㦬 㦭 㦮 㦯 㦰 㦱 㦲 㦳 㦴 㦵 㦶 㦷 㦸 㦹 㦺 㦻 㦼 㦽 㦾 㦿 㧀 㧁 㧂 㧃 㧄 㧅 㧆 㧇 㧈 㧉 㧊 㧋 㧌 㧍 㧎 㧏 㧐 㧑 㧒 㧓 㧔 㧕 㧖 㧗 㧘 㧙 㧚 㧛 㧜 㧝 㧞 㧟 㧠 㧡 㧢 㧣 㧤 㧥 㧦 㧧 㧨 㧩 㧪 㧫 㧬 㧭 㧮 㧯 㧰 㧱 㧲 㧳 㧴 㧵 㧶 㧷 㧸 㧹 㧺 㧻 㧼 㧽 㧾 㧿 㨀 㨁 㨂 㨃 㨄 㨅 㨆 㨇 㨈 㨉 㨊 㨋 㨌 㨍 㨎 㨏 㨐 㨑 㨒 㨓 㨔 㨕 㨖 㨗 㨘 㨙 㨚 㨛 㨜 㨝 㨞 㨟 㨠 㨡 㨢 㨣 㨤 㨥 㨦 㨧 㨨 㨩 㨪 㨫 㨬 㨭 㨮 㨯 㨰 㨱 㨲 㨳 㨴 㨵 㨶 㨷 㨸 㨹 㨺 㨻 㨼 㨽 㨾 㨿 㩀 㩁 㩂 㩃 㩄 㩅 㩆 㩇 㩈 㩉 㩊 㩋 㩌 㩍 㩎 㩏 㩐 㩑 㩒 㩓 㩔 㩕 㩖 㩗 㩘 㩙 㩚 㩛 㩜 㩝 㩞 㩟 㩠 㩡 㩢 㩣 㩤 㩥 㩦 㩧 㩨 㩩 㩪 㩫 㩬 㩭 㩮 㩯 㩰 㩱 㩲 㩳 㩴 㩵 㩶 㩷 㩸 㩹 㩺 㩻 㩼 㩽 㩾 㩿 㪀 㪁 㪂 㪃 㪄 㪅 㪆 㪇 㪈 㪉 㪊 㪋 㪌 㪍 㪎 㪏 㪐 㪑 㪒 㪓 㪔 㪕 㪖 㪗 㪘 㪙 㪚 㪛 㪜 㪝 㪞 㪟 㪠 㪡 㪢 㪣 㪤 㪥 㪦 㪧 㪨 㪩 㪪 㪫 㪬 㪭 㪮 㪯 㪰 㪱 㪲 㪳 㪴 㪵 㪶 㪷 㪸 㪹 㪺 㪻 㪼 㪽 㪾 㪿 㫀 㫁 㫂 㫃 㫄 㫅 㫆 㫇 㫈 㫉 㫊 㫋 㫌 㫍 㫎 㫏 㫐 㫑 㫒 㫓 㫔 㫕 㫖 㫗 㫘 㫙 㫚 㫛 㫜 㫝 㫞 㫟 㫠 㫡 㫢 㫣 㫤 㫥 㫦 㫧 㫨 㫩 㫪 㫫 㫬 㫭 㫮 㫯 㫰 㫱 㫲 㫳 㫴 㫵 㫶 㫷 㫸 㫹 㫺 㫻 㫼 㫽 㫾 㫿 㬀 㬁 㬂 㬃 㬄 㬅 㬆 㬇 㬈 㬉 㬊 㬋 㬌 㬍 㬎 㬏 㬐 㬑 㬒 㬓 㬔 㬕 㬖 㬗 㬘 㬙 㬚 㬛 㬜 㬝 㬞 㬟 㬠 㬡 㬢 㬣 㬤 㬥 㬦 㬧 㬨 㬩 㬪 㬫 㬬 㬭 㬮 㬯 㬰 㬱 㬲 㬳 㬴 㬵 㬶 㬷 㬸 㬹 㬺 㬻 㬼 㬽 㬾 㬿 㭀 㭁 㭂 㭃 㭄 㭅 㭆 㭇 㭈 㭉 㭊 㭋 㭌 㭍 㭎 㭏 㭐 㭑 㭒 㭓 㭔 㭕 㭖 㭗 㭘 㭙 㭚 㭛 㭜 㭝 㭞 㭟 㭠 㭡 㭢 㭣 㭤 㭥 㭦 㭧 㭨 㭩 㭪 㭫 㭬 㭭 㭮 㭯 㭰 㭱 㭲 㭳 㭴 㭵 㭶 㭷 㭸 㭹 㭺 㭻 㭼 㭽 㭾 㭿 㮀 㮁 㮂 㮃 㮄 㮅 㮆 㮇 㮈 㮉 㮊 㮋 㮌 㮍 㮎 㮏 㮐 㮑 㮒 㮓 㮔 㮕 㮖 㮗 㮘 㮙 㮚 㮛 㮜 㮝 㮞 㮟 㮠 㮡 㮢 㮣 㮤 㮥 㮦 㮧 㮨 㮩 㮪 㮫 㮬 㮭 㮮 㮯 㮰 㮱 㮲 㮳 㮴 㮵 㮶 㮷 㮸 㮹 㮺 㮻 㮼 㮽 㮾 㮿 㯀 㯁 㯂 㯃 㯄 㯅 㯆 㯇 㯈 㯉 㯊 㯋 㯌 㯍 㯎 㯏 㯐 㯑 㯒 㯓 㯔 㯕 㯖 㯗 㯘 㯙 㯚 㯛 㯜 㯝 㯞 㯟 㯠 㯡 㯢 㯣 㯤 㯥 㯦 㯧 㯨 㯩 㯪 㯫 㯬 㯭 㯮 㯯 㯰 㯱 㯲 㯳 㯴 㯵 㯶 㯷 㯸 㯹 㯺 㯻 㯼 㯽 㯾 㯿 㰀 㰁 㰂 㰃 㰄 㰅 㰆 㰇 㰈 㰉 㰊 㰋 㰌 㰍 㰎 㰏 㰐 㰑 㰒 㰓 㰔 㰕 㰖 㰗 㰘 㰙 㰚 㰛 㰜 㰝 㰞 㰟 㰠 㰡 㰢 㰣 㰤 㰥 㰦 㰧 㰨 㰩 㰪 㰫 㰬 㰭 㰮 㰯 㰰 㰱 㰲 㰳 㰴 㰵 㰶 㰷 㰸 㰹 㰺 㰻 㰼 㰽 㰾 㰿 㱀 㱁 㱂 㱃 㱄 㱅 㱆 㱇 㱈 㱉 㱊 㱋 㱌 					

	①	②	③	④	⑤
添加剤 (%)	処理 温度 (℃)	pH	全酸量	体積抵抗 率 ($\Omega \cdot \text{cm}$)	熱安定性
ケイ酸酸	330	7.4	54	11.3	12.0/188
ステレン	330	8.7	57	9.8	10.5/190
ビフェニル	350	9.2	61	7.1	10.5/187
アントラセン	350	9.1	65	7.1	10.5/189
ビスフェノールA	350	8.9	43	12.8	11.0/192
グリセロール/ステア ート	330	7.5	50	10.3	9.5/191
ポリステアレン	330	7.5	58	10.4	10.5/190
ステアリン酸モノステ アレート	330	7.8	75	3.9	9.5/190
ステアリン酸ステア リル	330	8.7	63	9.7	9.5/190
ステアリン酸モノステ アール	330	7.2	117	10.3	10.0/190
オクタデシル ステアレート	330	8.6	75	8.9	10.5/191
ジフェニルジ スルフィド	330	5.1	48	7.2	10.5/190
ペンゾチオ フェン	330	8.5	68	9.0	10.5/191
2-ナフチル チオール	330	9.1	61	8.5	10.5/191
2-メルカプト ペンゾチオ フェン	350	7.2	196	8.9	9.5/187

	①	②	③	④	⑤	
	添加剤 (%)	処理温度 (℃)	pH	全酸量	体積抵抗率 ($\Omega \cdot \text{cm}$)	熱安定性
⑥	テトラメチル ジスルフィド	350	8.7	60	12.3	10.0/190
	オクタデシル ステアレート	350	8.7	48	8.1	11.0/188
	1,5-ヘキサ ジオール	350	8.8	39	9.7	10.5/190

*Ammonia was supplied at 2.3 NL/h into a rotary kiln packed with 200 g of the CB.
 ** Treated by the same method as in the case of ammonia except that stearic acid was blended at 5%.

Key: 1 Additive (%)
 2 Treating temperature (°C)
 3 Total acid amount
 4 Volume resistivity ($\Omega \cdot \text{cm}$)
 5 Thermal stability
 6 Lutidine
 Stearyl amine
 Indole
 Hexamethylenediamine
 Triethanolamine

1,3-Diphenylguanidine
Ammonia*
Ammonia + stearic acid**
 ϵ -Caprolactam
Melamine
sym-Diphenylthiourea
L-glutamic acid
t-Stilbene
 α -Phenylcinnamic acid
Methyl cinnamate
Cinnamic acid
Styrene
Biphenyl
Anthracene
Bisphenol A
Glycerol monostearate
Tristearin
PEG monostearate
Stearyl ricinolate
Monomethyl maleate
Octadecyl thiodiglycolate
Diphenyl disulfide
Benzothiophene
2-Naphthalenethiol
2-Mercaptobenzothiazole
Tetramethylthiuram disulfide
Polyglycerol
1,6-Hexanediol